In a recent investigation by McLennan, Ainslie, and Fuller of the carbon vacuum arc Schumann spectrum, studied with a fluorite spectrograph, many wave-lengths were observed which did not come out on our plates. Only a few wave-lengths were common to the two investigations, and these are given in Table III. The agreement in the measurements, it will be seen, is only fair.

Too much reliance must not be placed on the results obtained in the present investigation, for no special effort was made to obtain absolutely pure metals for use in the arcs, and time was not available for refining the work. The best that can be said is that the same lines always appeared for different samples of the metal used.

On the Absorption Spectra and the Ionisation Potentials of Calcium, Strontium, and Barium.

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[Plates 4–6.]

I. *Introduction.*

In view of the probability that the ionisation potential of an element is connected by the quantum relation $\nu = (1.5, \mathrm{S} \times h)/e$ with the characteristic spectral frequency $\nu = (1.5, \mathrm{S})$, it has become desirable to determine the value of this frequency for as many of the elements as possible. Its value, moreover, is best found by identifying the members of the series $\nu = (1.5, \mathrm{S}) - (m, \mathrm{P})$ in a spectrum and then calculating the limiting frequency of the series. Dunz, in his Inaugural Dissertation, gives the wave-lengths of several members of the series $\nu = (1.5, \mathrm{S}) - (m, \mathrm{P})$ for each of the elements mercury, zinc, and cadmium; and Lorenser, in his Inaugural Dissertation, gives the wave-lengths of a number of the members of the same series for magnesium, calcium, and strontium. Lorenser, however, while giving $\nu = 5535.69$ Å.U. as the wave-length of the first member of the series $\nu = (1.5, \mathrm{S}) - (m, \mathrm{P})$, for barium, states that the remaining members of the series are not known.

Starting at this point, we recently investigated the spectrum of barium,

and, as a result, have identified and measured the wave-lengths of the first ten members of the above-mentioned series. The following paper gives a short account of the experiments which enabled us to make this advance.

It was evident at the beginning of the work that some knowledge as to the identity of the wave-lengths of the series might be found by a study of (1) the Zeeman effect, (2) the spectrum of the element produced by the electronic bombardment of its vapour, (3) its Bunsen-flame spectrum, and (4) the absorption spectrum of its vapour. Of these the last mentioned seemed the most promising line of attack, and was followed up. Preparatory to investigating the spectrum of barium, some preliminary experiments were made with calcium and with strontium, and it was through the successful termination of this work that the way was opened up for making progress with barium.

In taking the photographs of the spectra, a large Hilger quartz spectrograph, type C, was used. This instrument gave a fairly high dispersion and had a range from $\lambda = 8000$ Å.U. to $\lambda = 2000$ Å.U. The plates used were the Wratten and Wainwright panchromatic plates made by the Eastman Kodak Company, of Rochester, N.Y., which were sensitive up to about $\lambda = 7500$ Å.U., with fairly short exposures. For work in the red region of the spectrum, Schumann plates were sensitised with the sensitiser recently put on the market by the Adam Hilger Company. These plates were found to be just as sensitive in the red as the panchromatic plates, and gave perhaps slightly clearer definition. For the work in the ultra-violet region the ordinary Schumann plates were used.

II. *Absorption Spectrum of Calcium.*

A. S. King,[*] who investigated the emission spectrum of calcium in the electric furnace, found that the reversal of the calcium line $\lambda = 4226 \cdot 91$ Å.U. did not begin until a temperature between 2500° C. and 3000° C. was reached. This fact at once showed that absorption with calcium could not be studied by vapourising the metal in an exhausted quartz tube in the manner previously carried out by one of us with mercury, zinc, or cadmium. With strontium and barium, though the temperature necessary to produce vapourisation is not so high as for calcium, other difficulties were met, which precluded the use of the ordinary method. Hot quartz was found to be very readily attacked by all three of the metals, calcium, strontium, and barium, which formed an opaque silicate and soon rendered an absorption tube useless. Metallic strontium and barium, moreover, are rare and costly.

* A. S. King, 'Astrophys. Jour.,' vol. 28, p. 389 (1908).

To obviate these difficulties and to obtain the high temperature necessary, the ordinary carbon arc was utilised, with a current of 15–20 ampères. Two solid commercial carbons were taken and the vertical one was bored out for a considerable part of its length and filled with calcium metal. The ends were kept blunt, so that the arc could be struck at the edges of the carbons. The vertical carbon was made positive, and, as it got hot, the calcium metal vapourised and passed up in front of the arc, the light from which was focussed on the slit of the spectrograph with a cylindrical quartz lens. Visual observation with a small glass spectroscope showed that ready absorption took place at the wave-length $\lambda = 4226 \cdot 91$ Å.U., and photographs taken with the various types of plates mentioned above showed that, under suitable conditions, it was possible to obtain either the emission spectrum of calcium or the absorption spectrum, in which the reversals were confined entirely to those wave-lengths which were members of the series $\nu = (1 \cdot 5, \text{S}) - (m, \text{P})$. As given by Lorenser, these are :—

$m =$	2	3	4	5	6
$\lambda =$	$4226 \cdot 91$	$2721 \cdot 77$	$3298 \cdot 66$	$2275 \cdot 60$	$2200 \cdot 8$

$m =$	7	8	9	10	11
$\lambda =$	$2151 \cdot 00$	$2118 \cdot 99$	$2097 \cdot 8$	$2083 \cdot 2$	$2072 \cdot 8$

In most of our plates the absorption at $\lambda = 2721 \cdot 77$ Å.U. was weak, and in some plates it could not be detected at all. For the other members of the series the absorption was very marked.

The first spectrum on Plate 4 is the emission spectrum of calcium in the carbon arc, the second the absorption spectrum on a panchromatic plate, the third the absorption spectrum on a Schumann plate, and the fourth the emission spectrum of the carbon arc alone.

III. *The Absorption Spectrum of Strontium.*

In the case of strontium exactly the same experimental arrangements were used, but in place of the metal the sulphide of strontium was used. It was expected that in the heat of the arc the salt would become dissociated, and the free metal obtained in the form of vapour. This proved to be the case. Absorption at $\lambda = 4607$ Å.U. was observed visually, and at times was very broad, the band appearing to be symmetrically spaced, as was the case with the calcium absorption band at $\lambda = 4226$ Å.U. The photographs, moreover, revealed absorption at a number of places, which, on being measured up, agreed exactly with the values of the series frequencies given

for $\nu = (1\cdot5, \text{S}) - (m, \text{P})$ by Lorenser. In all, 10 absorption bands were found corresponding to values of m given below :

$m =$	2	3	4	5	6
$\lambda =$	4607·52	2931·98	2569·60	2428·16	2354·40

$m =$	7	8	9	10	11
$\lambda =$	2307·5	2275·5	2253·5	2237·4	2226·0

The reproductions shown in Plate 5 are (*a*) the emission spectrum of strontium in the carbon arc taken with a sensitised Schumann plate, (*b*) the absorption spectrum of strontium with a panchromatic plate, (*c*) the absorption of the metal with an ordinary Schumann plate, and (*d*) the spectrum of the carbon arc alone.

IV. *Absorption Spectrum of Barium.*

From the results obtained with calcium and strontium, it was evident that we had, in the use of the carbon arc, a promising means of spotting at once, by noting reversals, the members of the series $\nu = (1\cdot5, \text{S}) - (m, \text{P})$. On trying out the method with barium, the results sought for came immediately. The oxide of the metal was used in this case. Visual observation showed that absorption in the visible region occurred at $\lambda = 5535\cdot69$ Å.U., but the reversal was much narrower than in the case of calcium at $\lambda = 4227\cdot91$ Å.U., or of strontium at $\lambda = 4607$ Å.U. This, no doubt, was what might have been expected, for the line $\lambda = 5535\cdot69$ Å.U. in emission in the barium spectrum is much narrower than either of the corresponding ones in the spectra of calcium and strontium. As stated above, the lines of the series given by $\nu = (1\cdot5, \text{S}) - (m, \text{P})$ for barium other than the first members were not known, but by analogy with the absorption spectra of calcium and strontium it was expected that the absorption of barium would be confined to the members of this series. Many photographs were taken, and while some showed only the emission spectrum of barium, others showed a converging series of clear and distinct reversals.

Plate 6 shows (*a*) the emission spectrum of barium in the carbon arc taken with a sensitised Schumann plate, (*b*) the absorption spectrum of barium with a panchromatic plate, (*c*) the absorption spectrum of the metal with a Schumann plate, and (*d*) the carbon arc spectrum.

The wave-lengths of the lines which showed absorption were carefully measured, and in all nine members were noted. The values of the wave-lengths as measured are :—

$m =$	2	3	4	5	6
$\lambda =$	5535	3275	2845	2597	2542
$\nu =$	10864·6	30534·4	35149·4	38502·1	39339·1

$m =$	7	8	9	10
$\lambda =$	2498	2470	2455	2441
$\nu =$	40032	40486	40733·2	40966·8

From the location and distribution of these lines in the spectrum, coupled with the fact that the initial line showing absorption is $\lambda = 5535\cdot69$ Å.U., it would seem clear that we have in them the first nine members of the series $\nu = (1\cdot5\ S) - (m,\ P)$ for the spectrum of barium. Their frequencies, which have been calculated, are given above.

V. *Series Lines and their Frequencies.*

(*a*)
$$\nu = (1, 5, S).$$

If our assumption be correct, the wave-lengths just given constitute the first nine numbers of the series whose frequencies are represented by $\nu = (1\cdot5,\ S) - (m,\ P)$. It follows, by selecting the frequencies for which $m = 9$ and 10, that the frequency $\nu = (1\cdot5,\ S)$ is numerically given by $42006\cdot85$. The wave-length corresponding to this frequency, which is $\lambda = 2380\cdot56$ Å.U., is therefore the limiting one for the series $\nu = (1\cdot5, S) - (m,\ P)$.

(*b*)
$$\nu = (m,\ P).$$

Since the frequency $\nu = (1\cdot5,\ S)$ is known, it follows that the frequencies given by $\nu = (m,\ P)$ can be easily calculated.

They are as follows :—

$m =$	2	3	4	5	6
$m,\ P =$	23942·25	11472·45	6857·45	3504·75	2667·75

$m =$	7	8	9	10
$m,\ P =$	1974·85	1520·85	1273·35	1040, etc.

(*c*)
$$\nu = (2\cdot5, S) \quad \text{and} \quad \nu = (3\cdot5, S).$$

The frequencies $\nu = (2\cdot5,\ S)$ and $\nu = (3\cdot5,\ S)$ can also be calculated with a fair degree of accuracy, and are given below :

$m =$	2·5	3·5
$(m,\ S) =$	16148	8436·5 etc.,
$\lambda =$	6192·7	11852·5

(*d*)
$$\nu = (2\cdot5, S) - (m,\ P) \quad \text{and} \quad \nu = (3\cdot5, S) - (m,\ P).$$

With the constituent elements given above available, it follows that the

frequencies of the two series $\nu = (2\cdot5, \text{S})-(m, \text{P})$ and $\nu = (3\cdot5, \text{S})-(m, \text{P})$, and their corresponding wave-lengths, are :—

1. $\nu = (2\cdot5, \text{S}) -(m, \text{P})$

$m =$	2	3	4	5
$\nu =$	7794	4676	9291	12·644
$\lambda =$	12830·0	21390	10763·1	7908·8 etc.

2. $\nu = (3\cdot5, \text{S})-(m, \text{P})$

$m =$	2	3	4	5
$\nu =$	15055	3035	1580	4933
$\lambda =$	6742·3	32949	63291	20271·7

From the data at present available, it is not clear whether the frequencies as calculated have a real existence or not in the spectrum of barium.

Randall* gives strong lines at $\lambda = 10034\cdot8$ Å.U., $\lambda = 10650\cdot5$ Å.U., and $\lambda = 12084$ Å.U., and the frequencies of the last two of these lines approximate to the calculated values of $\nu = (2\cdot5, \text{S})-(4, \text{P})$ and $\nu = (2\cdot5, \text{S})-(2, \text{P})$, respectively. The agreement, however, is not good.

(e) $\qquad\qquad \nu = (1\cdot5, \text{S})-(2, p_2).$

The value of the frequency $\nu = (2, p_2)$ which is given by Dunz as $29350\cdot4$ leads to the value of $12656\cdot45$ for $\nu = (1\cdot5, \text{S})-(2, p_2)$. The wave-length corresponding to this frequency is $\lambda = 7901\cdot11$ Å.U. Saunders† includes in his list a comparatively strong line at $\lambda = 7906\cdot13$ Å.U., but this line does not appear to exhibit absorption and other effects such as one should expect to be associated with a line of the frequency $\nu = (1\cdot5, \text{S})-(2, p_2)$.

VI. *Ionisation Potential.*

In a recent paper by Bergen, Davis, and Goucher,‡ an account is given of some experiments with mercury vapour which go to show that when electrons having a velocity corresponding to a fall of potential of between 10 and 11 volts are allowed to bombard the vapour in a high vacuum, they are just able to produce a definite and distinct type of ionisation. Tate and Foote§ have also recently described some experiments with the vapour of cadmium and zinc which led them to the conclusion that the ionisation potentials for the vapours of these two metals are respectively 8·92 volts and 9·5 volts.
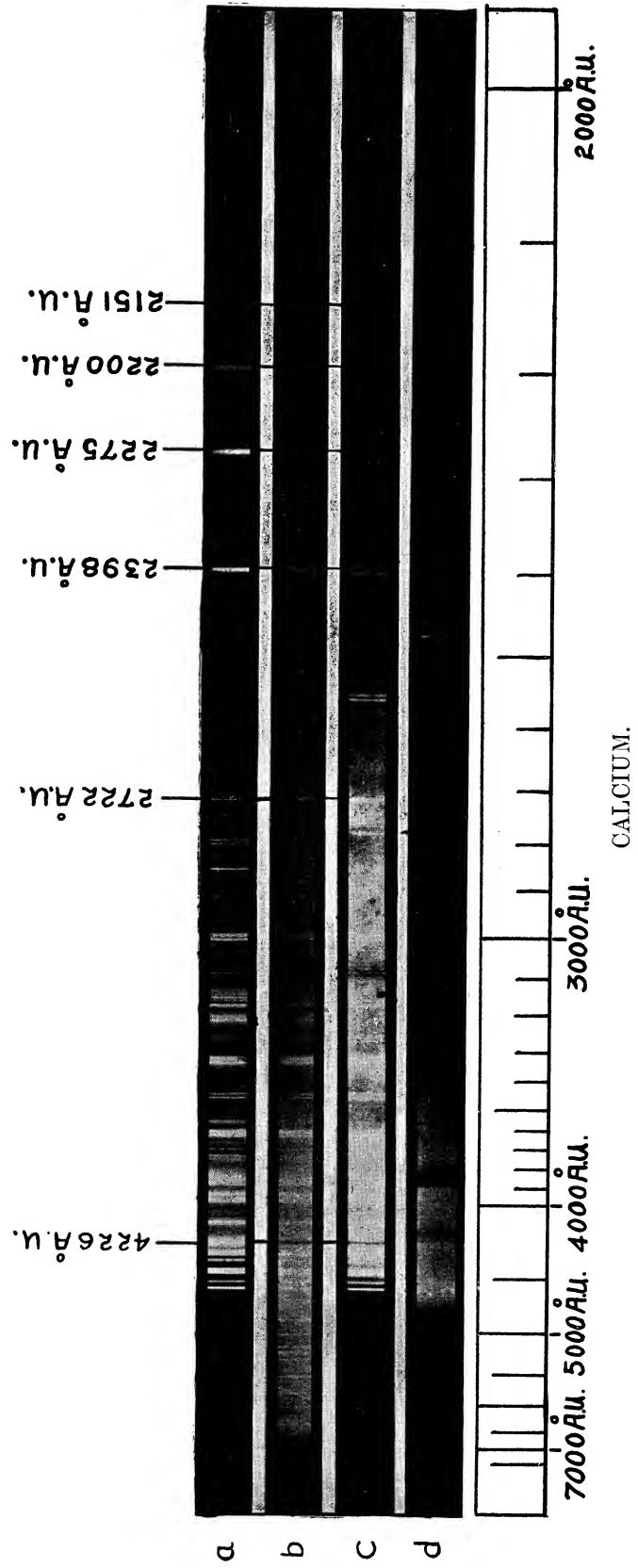
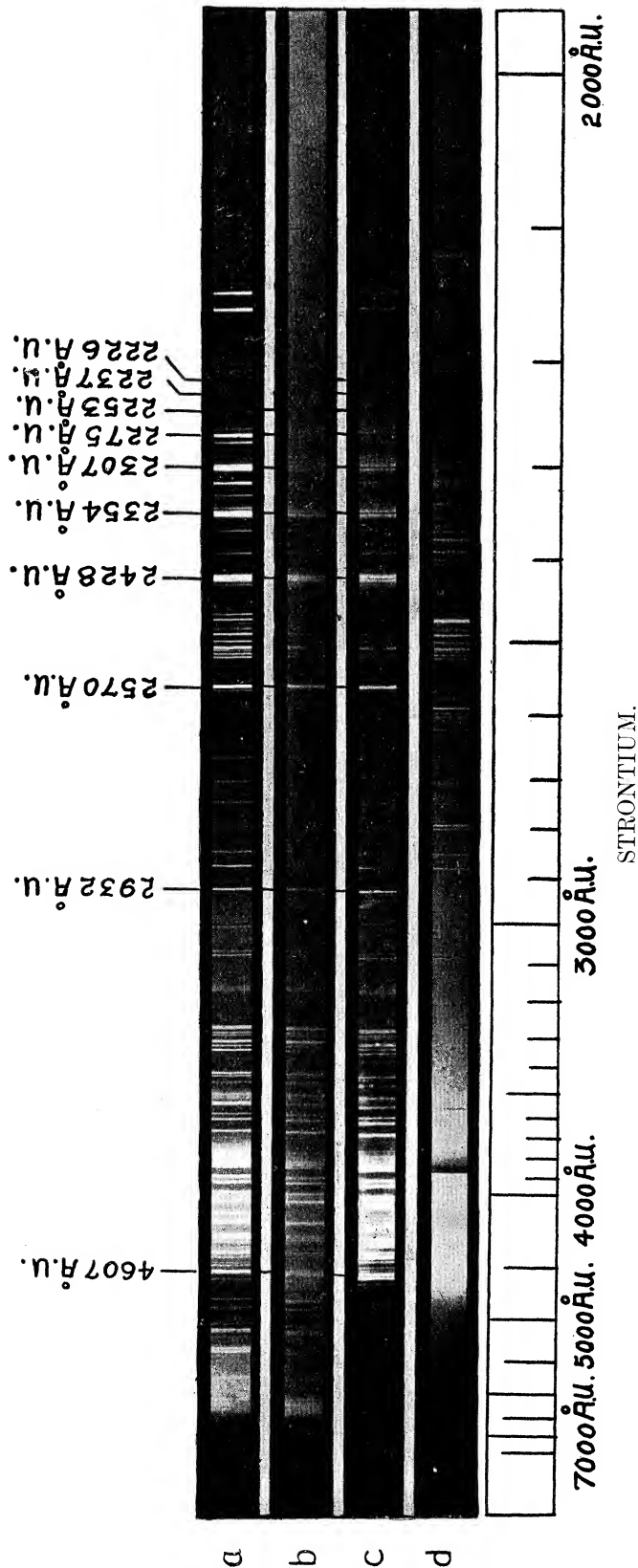These experimental results therefore constitute a confirmation of the view

* H. M. Randall, 'Ann. der Phys.,' vol. 33, pp. 739–746 (October 25, 1910).
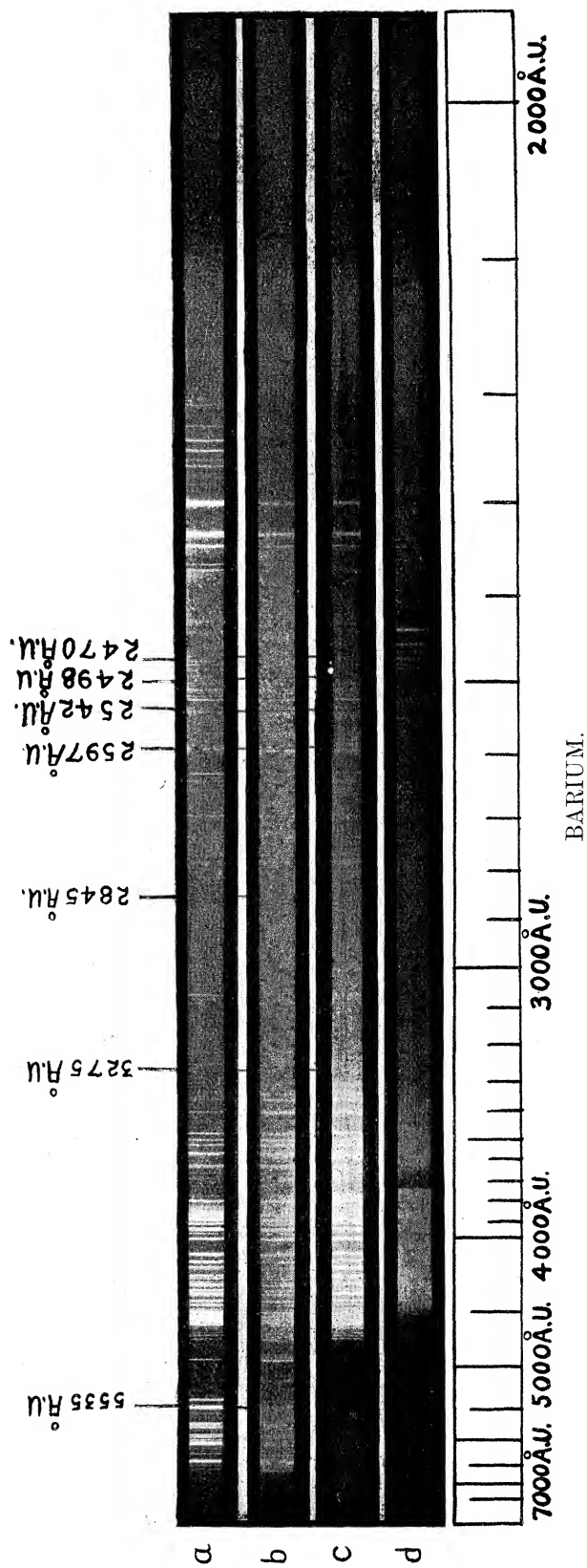† Saunders, 'Astrophys. Jour.,' vol. 32, No. 2, p. 155 (September, 1910).
‡ Bergen, Davis, and Goucher, 'Phys. Rev.,' August, 1917.
§ Tate and Foote, 'Phil. Mag.,' July, 1918, p. 88.

McLennan and Young.

CALCIUM.

McLennan and Young.

Roy. Soc. Proc., A, vol. 95, Pl. 5.

4607 Å.u.

2932 Å.u.

2570 Å.u.

2428 Å.u.

2354 Å.u.

2307 Å.u.
2275 Å.u.
2253 Å.u.
2237 Å.u.
2226 Å.u.

a

b

c

d

STRONTIUM.

7000 Å.u. 5000 Å.u. 4000 Å.u. 3000 Å.u. 2000 Å.u.

Roy. Soc. Proc., A, vol. 95, Pl. 6.

McLennan and Young.

BARIUM.

put forward by one of the writers in a series of communications,* that ionisation potentials for the atoms of mercury, zinc, cadmium, magnesium, and possibly also for those of other elements are given by the quantum relation $Ve = h\nu$, where ν is given by the frequency relation $\nu = (1 \cdot 5, S)$. This view, it should be stated, was reached from experiments carried out at Toronto on (1) single line emission spectra, (2) the absorption spectra of metallic vapours, (3) arcing potentials in metallic vapours, and (4) from considerations connected with the theory of atomic structure developed by Bohr.

If we accept this view as correct, it follows, if it be of general application, that ionisation potentials may be calculated for those elements for which the spectral frequency $\nu = (1 \cdot 5, S)$ is known.

From the data now available, including that for barium, these have been calculated, assuming $h = 6 \cdot 585 \times 10^{-27}$ erg. sec., and $e = 4 \cdot 774 \times 10^{-10}$ e.s.u., and are given in Table I.

Table I.

Element.	$\lambda \ (\nu = 1 \cdot 5, S)$.	Ionisation potential calculated from $V = \dfrac{(1 \cdot 5, S) h}{e}$.
	A.U.	volts.
Mercury	1187 ·98	10 ·45
Zinc	1319 ·95	9 ·4
Cadmium	1378 ·69	9 ·0
Magnesium	1621 ·7	7 ·65
Calcium	2028 ·2	6 ·12
Strontium	2177 ·5	5 ·7
Barium	2380 ·56	5 ·21

The experiments of Tate and Foote point the way for a direct determination of the ionisation potentials of the vapours of magnesium, calcium, strontium, and barium, and it will be interesting to see whether experimental values so obtained for these vapours agree with the values calculated above from the limiting frequencies of the singlet series of their spectra.

* McLennan and Henderson, 'Roy. Soc. Proc.,' A, vol. 91, p. 485 (1915) ; McLennan, 'Roy. Soc. Proc.,' A. vol. 92, p. 305 (1915); McLennan, 'Jour. Franklin Institute,' February, 1916, p. 191 ; McLennan, 'Roy. Soc. Proc.,' A, vol. 92, p. 574 (1916).

CALCIUM.
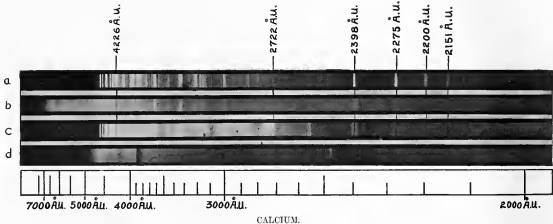
4607 Å.u.   2932 Å.u.   2570 Å.u.   2428 Å.u.   2354 Å.u.   2307 Å.u.   2275 Å.u.   2255 Å.u.   2237 Å.u.   2226 Å.u.

a

b

c

d

7000 Å.u. 5000 Å.u. 4000 Å.u.   3000 Å.u.   2000 Å.u.

STRONTIUM.

5555 Å.u.　　　3275 Å.u.　　2845 Å.u.　　2597 Å.u.　2542 Å.u.　2498 Å.u.　2470 Å.u.

a

b

c

d

7000Å.U. 5000Å.U. 4000Å.U.　　3000Å.U.　　　　　　　　　　2000Å.U.

BARIUM.